Aggregation-induced emission of tetraphenylethylene-modified polyethyleneimine for highly selective CO_2 detection

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A B S T R A C T

A polymer-based visible and quantitative fluorometric assay for CO_2 gas is constructed using branched polyethyleneimine (PEI) covalently modified with tetraphenylethylene (TPE). The sensing mechanism relies on the reaction of CO_2 with alkylamines of PEI to induce the "solution-to-precipitation" phase transition of the sensory polymer (TPE–PEI), thus resulting in strong aggregation-induced fluorescent emission of TPE–PEI. It works in a relatively environmental benign ethanol medium and avoids the use of toxic amine compounds with unpleasant odor. More importantly, this system is proved to be highly tolerant to possibly coexisting water, carbon monoxide, acid SO_2 and H_2S gases as well as many common volatile organic compounds. These characteristics make the presently developed fluorescent chemosensor hold great potential for many real-world applications.

Keywords:
Aggregation-induced emission
Carbon dioxide
Fluorescent sensor
Polyethyleneimine
Tetraphenylethylene

1. Introduction

CO_2 detection is of fundamental importance for a diverse array of real-world applications. For example, high concentration of CO_2 (>20%) is widely used in modified-atmosphere packaging for non-respiring food, and a decrease in CO_2 levels is a sign of leakage in a package [1]. Detection of extreme levels of CO_2 can ensure the safety of farmers and workers in agricultural-confined spaces (e.g., manure storage facilities and grain silos) and low-lying mines, wells, tunnels, sewers, where significantly elevated concentration of CO_2 was usually reported due to its higher density than air [1]. It is also helpful for disaster prediction and prevention by daily monitor of the CO_2 content in gas mixtures released by dormant craters (typically containing 10–40% of CO_2) [2].

Conventional strategies for CO_2 sensing include infrared (IR) and electrochemical (EC) methods [1], Severinghaus type potentiometric sensors [3], gas chromatography–mass spectrometry [4]. However, these methods generally rely on expensive and bulky instruments and are not suitable for on-site analysis in some cases. Especially, both IR and EC methods are severely subject to interference from water vapor that is almost ubiquitous everywhere [2]. Newly developed field-effect transistors [5–9] and surface plasmon resonance-based sensors [10] are promising, but have not been widely used so far because of complicated processes or expensive equipments.

As an alternative to these methods, optical gas probes [10–24], depending on CO_2-induced changes in absorbance and fluorescence, are attracting increasing attention owing to their simple and low-cost construction, fast response and ability to conduct real-time measurements. Up to now, a large number of optical sensors have been reported. However, most of these probes rely primarily on the acidic properties of CO_2 and are thus possibly cross-sensitive to the coexisting volatile acid sulfur-bearing gases (SO_2, H_2S, etc.). Another strategy was based on the chemical reaction of primary amines and CO_2 to produce the corresponding ammonium carbamate salts [25–29]. Several colorimetric or fluorescent sensors involving this chemical mechanism have been achieved based on chromophoric moieties such as pyrene [30] or polydiacetylene [31]. Besides, two CO_2 sensing schemes were also constructed on the basis of altering the novel photophysical effect of AIE (Aggregation-induced emission)-active fluorogens [2,32]. Unlike traditional aggregation-caused quenching (ACQ) molecules [33,34], typical AIE-active ones such as hexaphenylsilole (HPS) and tetraphenylethylene (TPE) are non-emissive in good solutions but highly luminescent as aggregates. Tang et al. [2] thus designed a CO_2 assay scheme over a wide concentration range, utilizing the dipropylamine solutions of HPS. The viscosity and polarity of the

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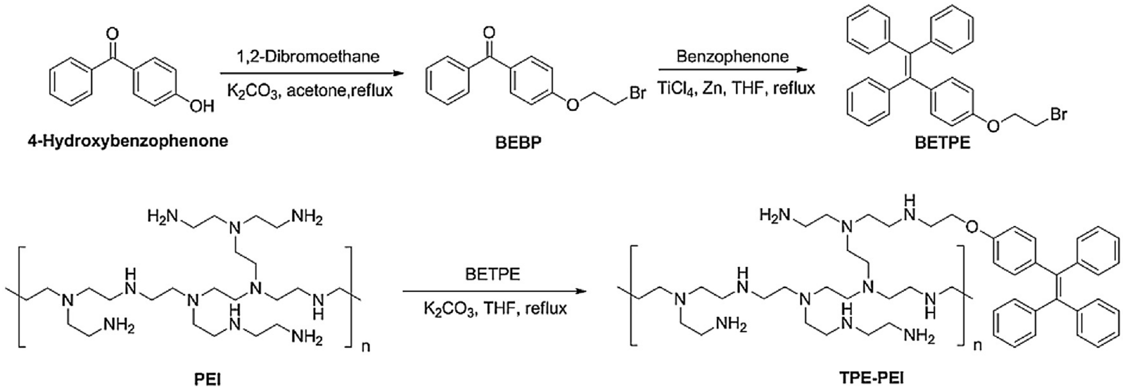

Scheme 1. The synthetic route of compound BETPE and the sensory polymer TPE–PEI.

solutions are significantly increased upon bubbling with CO_2, thus inducing the strong fluorescence emission of HPS. A similar but greener approach was subsequently reported by Tian et al. [32] where 5-amino-1-pentanol solutions of TPE with lower toxicity were used. However, these fluorescent sensory systems are still not perfect because toxic reagents with unpleasant odor (mainly amine compounds) are required. In addition, although both of these fluorescent probes are proved to have extraordinarily high water-resistance and no problem of carbon monoxide (CO)-interfering, whether they are also highly tolerant to possibly coexisting acid SO_2 and H_2S gases or common volatile organic compounds (alkanes, triethylamine, acetone, etc.) remains unknown. Therefore, it is of great urgency to develop a simple, quick, highly selective and quantitative method that is applicable in a relatively low environmental impact medium such as ethanol.

In our work, we report a visible and quantitative polymer-based "AIE" fluorescent chemosensor for CO_2 gas based on branched polyethyleneimine (PEI) covalently modified with tetraphenylethylene (TPE). Differing from the above mentioned two small molecules-based "AIE" fluorescent probes [2,32], this polymeric probe design relies on CO_2-induced "solution to precipitation" phase transition of the sensory polymer (TPE–PEI) solutions, thus enabling visible detection of CO_2 gas by naked-eyes and fluorescence-based quantification analysis. As shown in Fig. 1, when CO_2 gas is purged into the ethanol solutions of the TPE–PEI, the transparent solution will turn to turbid precipitation because of the fast reaction between the alkylamines of TPE–PEI and CO_2 to produce poorly-soluble polyammonium carbamate salts (TPE–PEI–CO_2) [35–37]. As a result, the light emission of TPE fluorogens is turned on for the restriction of intramolecular rotations (RIR) of its multiple phenyl rotors is activated in the suspension medium [2]. Moreover, the as-prepared sensory system is highly tolerant to various interferents including not only water and CO, but also acid SO_2 and H_2S gases as well as many common volatile organic compounds, suggesting the chemosensor that is described will have great potential real-world applications.

2. Materials and methods

2.1. Instruments

^{1}H NMR spectra were measured on a Bruker Advance AMX-400 spectrometer in $CDCl_3$ using tetramethylsilane as internal reference. Steady-state fluorescence spectra were recorded on a Hitachi F-4600 spectrofluorometer at controlled conditions (around 300 K and 1 atm) equipped with a Xe lamp (150 W) with an excitation wavelength of 350 nm. The slit widths were set at 10 nm for both excitation and emission. Particle size of the TPE–PEI aggregates in ethanol solution was determined using a Zetasizer Nano ZS particle size distribution analyzer (Malvern Instruments Ltd.). The optical micrographs of the aggregates were taken by a BX51-P Polarizing Microscope from Olympus Company.

2.2. Materials

Analytically pure reagents such as benzophenone, titanium tetrachloride, zinc powder, 1,2-dibromoethane, acetone, potassium carbonate, sodium sulphite, concentrated sulfuric acid, copper sulfide, anhydrous ethanol, dichloromethane, chloroform, triethylamine, hexane, ethyl acetate, tetrahydrofuran (THF) were purchased from Shanghai Sinopharm Chemical Reagent Co. 4-Hydroxybenzophenone and branched polyethyleneimine (PEI, $M_w \sim 10000$) were obtained from Energy Chemical Co. and Aladdin Shanghai Reagent Co., respectively. Sulfur dioxide gas was prepared by the reaction of sodium sulphite and concentrated sulfuric acid. Hydrogen sulfide gas was produced through the reaction of copper sulfide and diluted sulfuric acid. High-purity carbon dioxide and nitrogen gases were purchased from High Tech Zone Ningbo Nuoan Gas Ltd. Dry THF was distilled under N_2 protection after being treated by potassium. Acetone and ethanol were distilled under N_2 atmosphere before use.

2.3. Preparation of the sensory solutions and N_2/CO_2 gas mixtures

The solutions (ethanol, $CHCl_3$, 1-methyl-2-pyrrolidinone) of TPE–PEI with a concentration of 2.4 mg/mL were first prepared under N_2 protection and stored with seal at ambient conditions before use. The N_2/CO_2 gas mixtures with different content of CO_2 were prepared according to the reported method [29,38], which has been described in detail there.

2.4. Synthesis and characterization

Synthesis of 1-[4-(2-bromoethoxy)phenyl]-1,2,2-triphenylethylene (BETPE) [39,40]. Into a mixture of 4-hydroxybenzophenone (8.9 g, 50.0 mmol) and potassium carbonate (13.8 g, 100.0 mmol) in dry acetone (100 mL), excess 1,2-dibromoethane (20 mL, 229.0 mmol) was added under N_2 protection. After being refluxed under stirring for 24 h, the mixture was filtered. The solvent was evaporated under vaccum and the crude product was dissolved in ethyl acetate and washed with saturated sodium bicarbonate aqueous solution, brine and deionized water. Then the combined organic phase was dried by magnesium sulfate and concentrated under vaccum to afford BEBP (4-(2-bromoethoxy)-benzophenone) as a white solid in 95.8% yield (12.8 g) based on 4-hydroxybenzophenone. BEBP was used without further purification and characterization.

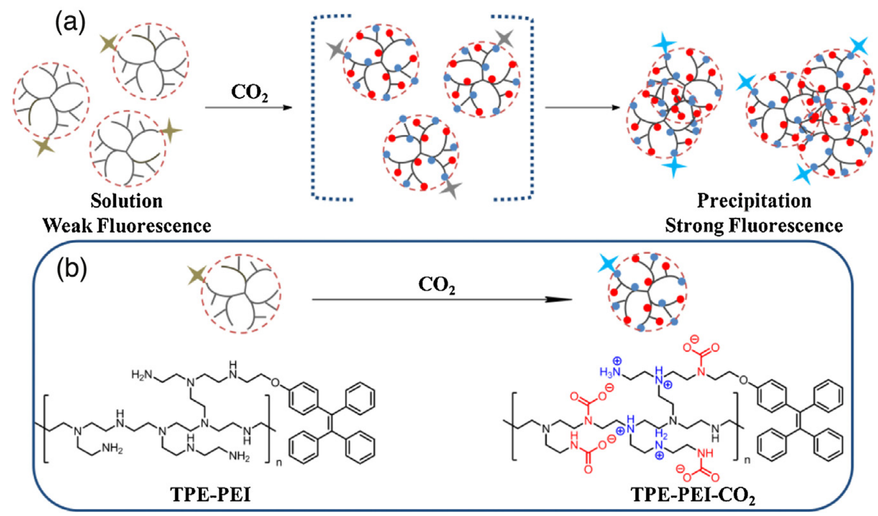

Fig. 1. (a) Schematic representation of the sensing process of the developed polyethyleneimine-based fluorescent sensory system covalently modified with a typical AIE-active TPE fluorogen; (b) Structure of the sensory polymer TPE–PEI and its chemical reaction with CO_2 to form polyammonium carbamates salts TPE–PEI–CO_2 at ambient conditions.

Under N_2 atmosphere, titanium tetrachloride (5.2 mL, 46.0 mmol) was added very slowly into a mixture of benzophenone (2.2 g, 12.0 mmol), BEBP (3.0 g, 10.0 mmol) and zinc (Zn) powder (2.0 g, 31.3 mmol) in 50 mL of dry THF in an ice bath. After being refluxed for 36 h, the reaction mixture was cooled to room temperature and 50 mL of saturated potassium carbonate aqueous solution was added. The precipitation was filtered and the solvent was removed under vaccum. Then the crude product was purified through a silica gel column using hexane as eluent to give BETPE as a white solid in 35% yield based on BEBP. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): 3.61 (2H, C**H**$_2$-Br), 4.23 (2H, C**H**$_2$-O), 6.68 (2H, Ar**H**), 6.98 (2H, Ar**H**), 7.02~7.18 (15H, Ar**H**).

Synthesis of tetraphenylethylene-modified polyethyleneimine (TPE–PEI) [41,42]. To a mixture of polyethyleneimine (2.0 g, $M_w \sim 10000$) and K_2CO_3 (0.5 g) in 30 mL of dry THF, BETPE (25.0 mg) was added under nitrogen atmosphere. After being refluxed for 8 h, the mixture was diluted with 50 mL ethanol and filtered twice to give a clear solution. The solution was then concentrated under vacuum. In order to completely remove the unreacted BETPE, the resulting mixture was poured into 200 mL hexane, which is good solvent for BETPE. The targeted polymer was dried under vacuum to give a pale yellow semisolid in 88% yield based on polyethyleneimine. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): 2.6 (N-C**H**$_2$, multiple strong peaks), 6.58 (Ar**H**, double weak peaks), 6.87 (Ar**H**, double weak peaks), 6.91–7.12 (Ar**H**, multiple weak peaks). See Fig. 2 for detailed information.

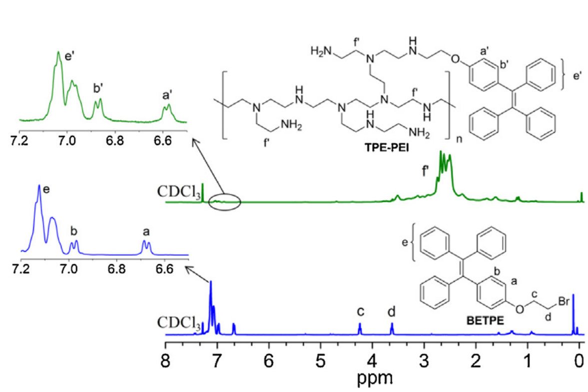

Fig. 2. ^{1}H NMR spectra of BETPE and TPE–PEI in $CDCl_3$.

3. Results and discussion

3.1. Synthesis and characterization of the sensory polymer

The synthetic procedure of TPE–PEI is illustrated in Scheme 1. BETPE (1-[4-(2-bromoethoxy)phenyl]-1,2,2-triphenylethylene) was first prepared through a facile two-step reaction and then allowed to react with commercially purchased PEI ($M_w \approx 10000$) to give TPE–PEI as a yellowish semisolid in high yield. As shown in Fig. 2, the typical resonance peaks at 6.5–7.2 ppm ascribed to aromatic protons of the TPE fluorogens is observed in the ^{1}H NMR spectrum of TPE–PEI, while, all the signal peaks of aromatic protons in TPE–PEI shift highfield about 0.1 ppm compared with those of BETPE in the same solvent ($CDCl_3$), indicating TPE molecules were successfully grafted onto PEI [41,42]. The resulting weight content of TPE moieties in TPE–PEI is calculated to be about 0.96% according to ^{1}H NMR spectrum[1]. Apparently, the content of TPE in the targeted sensory polymer is quite low so as not to affect distinctly the interaction of PEI with CO_2.

3.2. Detection of CO_2 gas

As mentioned above, TPE is not a traditional fluorogen and its fluorescence mechanism accords with a novel photophysical effect of aggregation-induced emission (AIE). Therefore, TPE–PEI is highly emissive as aggregates in solid state (Fig. S1) but almost non-emissive in various good solvents such as chloroform ($CHCl_3$), *N*-methyl-2-pyrrolidinone (NMP), ethanol and their mixtures (Fig. S1, S2(b) and 3(b)). Moreover, no noticeable changes were observed in the fluorescence and UV–vis spectra of these transparent sensory solutions even after long-time exposure to air (10 min) at ambient conditions. These observations demonstrate our sensory system is stable and non-sensitive to N_2, O_2 and extremely low concentration of CO_2 gas (390 ppm) in air. However, upon bubbling with only

[1] The general method to estimate the content of functional groups in the obtained polymer has been clearly described in the reference (see M.H. Gil, et al. Polymer, 46 (2005) 9604–9614). Herein, the weight content of TPE (WTPE) in the final polymer TPE–PEI is calculated using the following equation: $W_{TPE} = \left(\frac{I_{6.6}}{2} \times 332 / \frac{I_{2.6}}{4} \times 43 + \frac{I_{6.6}}{2} \times 332\right)$ where $I_{6.6}$ and $I_{2.6}$ are the integral of the peak at 6.6 and 2.6 ppm, respectively; 332 and 43 are the molecular weight of TPE ($C_{26}H_{20}$) and the monomer of PEI ($(CH_2CH_2NH)_n$), respectively.

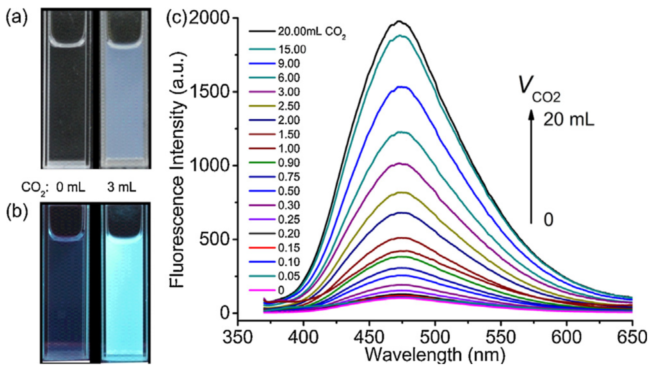

Fig. 3. (a) Photographs of TPE–PEI (2.4 mg/mL) in ethanol before and after being purged with 3 mL CO_2; (b) These photos were taken under UV illumination (365 nm); (c) Fluorescence response spectra of the ethanol solutions upon bubbling increasing volumes of CO_2 with excitation at 350 nm at controlled conditions (around 300 K and 1 atm).

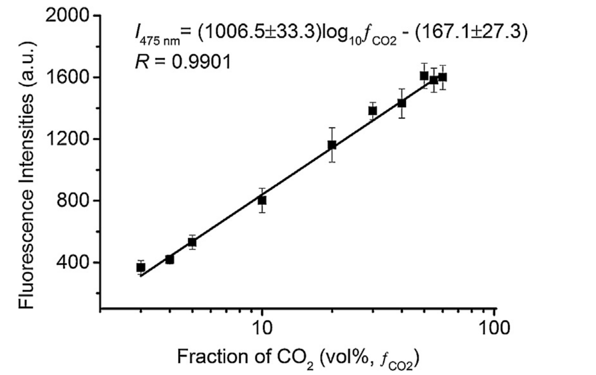

Fig. 4. The plot of fluorescence intensities of TPE–PEI (2.4 mg/mL) in ethanol at 475 nm versus the fraction of CO_2 $\left(f_{CO_2}\right)$ in N_2/CO_2 mixtures in the range from 3 to 60 vol%. The fluorescence intensities of the sensory solutions were recorded after being exposed to an atmosphere containing different CO_2–N_2 mixtures for 2 min. Excitation at 350 nm for fluorescence spectra measurement.

small volumes of pure CO_2 gas, a visible CO_2-induced phase transition of TPE–PEI is observed in these solutions by naked eyes. As shown in Figs. 3 (a) and S2, the solutions become turbid instantaneously after being purged with only 3 mL CO_2 gas. The phase transition process from transparent solution to turbid dispersion is sufficiently clear to the untrained for the unmistaken recognition of CO_2, indicating this sensing method is time-saving and will facilitate on-site decision-making. Meanwhile, these solutions emit intense blue emission under a UV lamp at 365 nm (Figs. S2 and 3(b)). This observation suggests that the fluorescence enhancement of TPE–PEI solutions does originate from the CO_2-induced aggregation of the sensory polymer. Further evidences come from dynamic light scattering (DLS) and microscopic analyses. As shown in Figs. S3 and S4, measurements with an optical microscope and particle size analyser reveal that the molecules of TPE–PEI were aggregated into micrometer-sized particles upon bubbling only 3 mL CO_2 gas into the ethanol solutions.

Considering that continuous excitation may result in the luminescent changes of fluorescent sensors, photostability of our sensory systems was then examined using the reported method [16], because high photostability will make a sensor suitable for long-duration measurements and validate the accuracy of quantitation. Thus, the transparent ethanol, $CHCl_3$ or NMP solutions of TPE–PEI (2 mL, 2.4 mg/mL) were first prepared under N_2 protection and sealed in quartz cuvettes with covers. The emission intensities of these sensory solutions were then monitored in a continuous irradiation at 350 nm for 500 s, which is sufficiently long to complete the whole measurement process. The results showed that no obvious change was observed in the fluorescence spectra, suggesting the good photostability of our sensory systems.

The CO_2-sensing ability of TPE–PEI was then systematically investigated in anhydrous ethanol solutions at controlled conditions (around 300 K and 1 atm). The main reason for choosing ethanol as the medium is its extremely low toxicity and environmental impact, considering that many potential “real-world” applications take place in agricultural-confined spaces (e.g., manure storage facilities and grain silos) or food packaging industry. For other possible applications, especially high temperature environments, *N*-methyl-2-pyrrolidinone (NMP, a solvent with high boiling point) solutions of TPE–PEI are recommended.

The fluorescence response spectra of the sensory ethanol solutions towards different volumes of pure CO_2 gas were then measured according to the reported method [2]. Typically, different volumes (0–20 mL) of pure CO_2 gas were extracted with a syringe and bubbled into the bottom of the TPE–PEI ethanol solution (2 mL in quartz cuvettes) through a 0.7 mm needle at a rate of about 10 mL/min without stirring at controlled conditions (around 300 K and 1 atm) [2,38]. It should be pointed out that no noticeable evaporation of the solvent (ethanol) was observed even after being bubbled with 20 mL CO_2 gas, validating the stability of the sensory solutions and the accuracy of measurements. The reaction between TPE–PEI and CO_2 went very fast in ethanol, as is evidenced by the observation that the photoluminescence intensities rapidly increase and nearly level off within only 2 min (Fig. S5). This fast spectroscopic response could provide the possibility of real-time quantitative detection. The fluorescence response spectra of the ethanol solutions of TPE–PEI to CO_2 were then recorded 2 min after being bubbled with increasing amount of CO_2 gas and shown in Fig. 3(c). Pristine TPE–PEI solutions are only weakly luminescent. Upon introduction of CO_2, fluorescence emission at 475 nm is significantly enhanced up to about 19-fold until signal saturation is reached.

It is of great practical value to quantify the fraction of CO_2 $\left(f_{CO_2}\right)$ in a gas mixture. N_2/CO_2 mixtures were then used as the model system in this work to study the fluorescence response of TPE–PEI solutions to variations of $\left(f_{CO_2}\right)$. All experiments were carried out in a 30 mL Schlenk flask. In a typical experiment, the flask was first subjected to vacuum in order to remove air and saturated with N_2 and CO_2 gas mixtures at controlled conditions (around 300 K and 1 atm). 1 mL anhydrous ethanol solutions of TPE–PEI (2.4 mg/mL) were then added quickly into the flask and vigorously stirred there at 1500 r/min before fluorescence measurement. Vigorous stirring of the sensory solutions was made to maximize the surface area for the reaction between CO_2 and the sensory solutions and shorten the equilibration time of the developed polymeric sensor, because the fabrication of a fast-response fluorescent probe is an essential prerequisite for real-time detection of CO_2. As expected, the time-dependent fluorescent response profiles (Fig. S6) showed that the fluorescence intensities at 475 nm rapidly increased and kept nearly constant after only 2 min within experimental error. Therefore, the fluorescence intensities of the sensory solutions were recorded after being exposed to an atmosphere containing different CO_2–N_2 mixtures for 2 min. As summarized in Fig. S7, the photoluminescence response of the sensory polymer at 475 nm is proportional to the amount of carbon dioxide present in the N_2/CO_2 gas mixtures and a LOD (limit of detection) of 1.2 vol% CO_2 is estimated according to the universal method for calculating the detection limit [43,44]. Importantly, a linear line (with a correlation coefficient 0.9901, see Fig. 4) was obtained for the semilog plot of the fluorescence intensities versus the fraction of CO_2 in the range of 3–60 vol%, thus enabling the quantification of CO_2 in various conditions, particularly for gas mixtures usually contain-

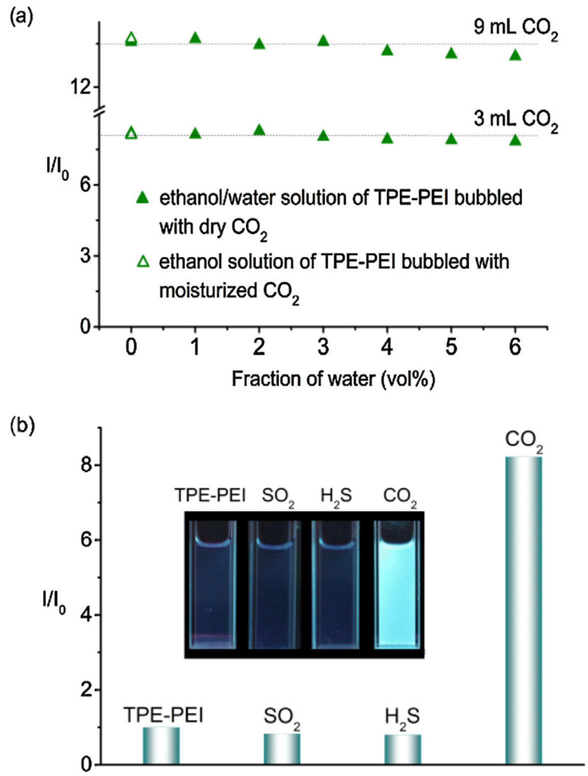

Fig. 5. (a) The plot of the relative fluorescence intensity changes (I/I_0) of TPE–PEI (2.4 mg/mL) in ethanol/water mixtures at 475 nm versus the fraction of water in the mixed solvent; (b) Fluorescence responses of TPE–PEI solutions at 475 nm upon bubbling with 3 mL of sulfurous gases (SO_2 and H_2S) and CO_2 with excitation at 350 nm. The photos were taken under a UV lamp at 365 nm.

ing significantly high CO_2 content in agricultural-confined spaces (manure storage facilities, grain silos, etc.) and low-lying mines, wells, tunnels, sewers [1].

Since the conventional sensing techniques (e.g., IR and EC sensors) have been reported to be cross-sensitive to water that usually coexists with CO_2, the effect of water on the performance of TPE–PEI was then examined using the reported method [2]. As displayed in Fig. 5(a), the fluorescence intensities of TPE–PEI solutions measured after being introduced with moisturized CO_2 are nearly identical to those recorded by using dry CO_2 as the bubbling gas. Furthermore, the data collected from the ethanol/water solutions of TPE–PEI with water content up to 5 vol% are almost the same as those obtained in dry ethanol within experimental error (the fluorescence loss is less than 4.5% even after 100 μL water was added into 2 mL anhydrous ethanol solutions of TPE–PEI), demonstrating the performance of TPE–PEI is little affected by the presence of water. Because another possible interferer, CO, does not react with amine groups, TPE–PEI is also free of CO-interfering problem [45,46]. Similarly, no fluorescence changes were noticed when exposure to air (containing about 78 vol% N_2 and 21 vol% O_2). Furthermore, no noticeable fluorescence enhancement was observed in the presence of many common volatile organic compounds (VOCs) such as ether, tetrahydrofuran, chloroform, acetone, ethanol, methanol, toluene, xylene, triethylamine, especially typical alkanes such as hexane and cyclohexane (up to 10,000 ppm in air). The good anti-interference ability of the presently developed sensory system towards alkanes is of great interest because there is a growing market for a cheap and reliable sensor of medium precision for the product quality monitoring of biogas, which is primarily composed of CO_2 and alkanes (mainly methane) [47].

To further prove its practical use in more complicated and varying testing environments such as volcano gas mixtures containing sulfur-bearing gases (SO_2, H_2S, etc.), control experiments to investigate the fluorescence response of TPE–PEI towards SO_2 and H_2S were then conducted and the results are summarized in Fig. 5(b). It is found that no obvious fluorescence increment was observed when 3 mL of these sulfurous gases were injected into the anhydrous ethanol solutions of TPE–PEI, indicating the presently developed "AIE" fluorescent polymeric sensor is highly tolerant to the coexisting sulfur-bearing gases. The excellent selectivity of TPE–PEI in ethanol over SO_2 and H_2S is easily understood for the following reasons. These sulfurous gases only produce molecular species (i.e., [$R_2NH\cdots SO_2$]) [48] with TPE–PEI rather than the formation of polyammonium carbamates salts when they are bubbled into the sensory solutions. As a result, aggregation-induced phase transition of the sensory polymer, which is responsible for the intense emission of the AIE-active TPE fluorophores, does not appear.

4. Conclusions

In conclusion, we have constructed a simple but highly selective fluorescent polymeric chemosensor for CO_2 gas based on the reaction of alkylamines with CO_2 to induce visible "solution-to-precipitation" phase transition. Its capacity to conveniently conduct both quick naked-eye distinction of CO_2 and fluorescence-based quantification of its amount is very attractive and distinguish the presently sensory system from alternative detection strategies. What's more, our sensory system works in a low environmental impact and nearly nontoxic solvent (ethanol) and is free of water, CO, SO_2, H_2S gases and volatile organic compounds-interfering problems often encountered in the traditional sensing techniques (e.g., IR and EC methods) or optical probes based on pH-sensitive fluorescent dyes. All of these characteristics make this sensing scheme hold potential for on-site analysis of the gas mixtures with high CO_2 contents in related fields, e.g., composition analysis of biogas, leak indicators for food packages, or disaster prevention in seismology and volcanology.

Acknowledgements

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.snb.2016.01.096.

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